Condensed tannin-sulfonate derivatives in cold-setting wood-laminating adhesives

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Abstract

Extraction of southern pine bark with 4.0 percent sodium sulfite and 0.4 percent sodium carbonate (based on ovendry bark weight) gives epicatechin-(4β)-sulfonate and oligomeric procyanidin-4-sulfonates that show great promise to replace about 50 percent of the phenol-resorcinol-formaldehyde resin in cold-setting wood-laminating adhesives. Bonds in Douglas-fir laminates exceed the minimal shear strength and wood failure requirements of the American Institute of Timber Construction Standards for dry shear (AITC-T107) and vacuum-pressure cold-water soak (AITC-T110) tests.

Condensed tannin-sulfonates can be obtained from southern pine bark at a cost of about $0.20/lb. Extract yields are about 20 percent of dry-bark weight when whole bark is extracted with sodium sulfite and sodium carbonate (6). In the course of this extraction, comparatively high molecular weight polymeric procyanidins (4,9,14) undergo cleavage at the interflavanoid bond to produce epicatechin-(4β)-sulfonate and oligomeric procyanidin-4-sulfonate derivatives (3). This reduction of molecular weight, with retention of phloroglucinol functionality, affords a product that is more suitable for use in wood-laminating adhesives than either neutral-solvent extracts that contain significant amounts of carbohydrates or dilute sodium hydroxide extracts that have undergone significant rearrangement and loss of phloroglucinol functionality (7,11). It has long been assumed that the presence of sulfonic acid functions in these tannin extracts would result in polymers that would be too soluble in water to provide water-resistant adhesive bonds (8,13). However, the sulfonate function in sodium epicatechin-(4β)-sulfonate is an extremely good leaving group in alkaline solutions at ambient temperature (5,11). Therefore, it should be possible to produce water-insoluble polymers that can be cured at ambient temperature by using condensed tannin-sulfonate intermediates. Tannin-based, wood-laminating adhesives, somewhat analogous to the wattle-tannin adhesives widely used in South Africa (12) but using comparatively inexpensive sulfite extracts from conifer barks, seem possible. Preliminary tests of this hypothesis have shown that tannin-sulfonates from southern pine bark have excellent potential for replacing at least 50 percent of the phenol-resorcinol-formaldehyde (PRF) resins commonly used in wood-laminating adhesives.

Experimental

Extraction and extracts used

Two types of tannin-sulfonate derivatives were prepared from extracts obtained by refluxing 100 parts by dry weight of finely ground southern pine bark (the whole bark obtained from trees about 30 years old) with 4.0 parts of sodium sulfite plus 0.4 parts of sodium carbonate in 600 parts of water for 2 hours.

One sample (A) was concentrated on a rotary evaporator, dialysed against distilled water overnight in Dialya-por C[1] membranes and the retentate was freeze-dried. A second sample (B) was made by concentrating the total extract to about 5 percent solids and drying it on a roller-drier without additional treatment.

Extract and resin solubility

Portions of each extract (A or B) were added stepwise to 10 g of water in 1 g lots up to a total of 7 g, giving a solids content of 41 percent. Aliquots from these solutions (0.5 g each) were combined with 50 percent sodium

[1]Mention of trade names does not constitute endorsement by the USDA-Forest Service.

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hydroxide solutions (0.04 g) and stirred to obtain a smooth solution. Then 0.50 g of a modified commercial PRF adhesive (Borden's LT-75 system[1] plus 10% of paraformaldehyde) was added. After allowing the hardened adhesive to stand as a solid at room temperature for 2 days, 10 ml of water was added. The color of the supernatant was evaluated after 3 to 4 weeks of standing at room temperature.

Gel time and adhesive formulation

A portion of each of the extracts A or B (0.5 g of 41% solutions) was combined with 50 percent sodium hydroxide (0.04 g) and a commercial PRF adhesive (0.50 g). The modified commercial PRF adhesive in this instance was made by combining Borden's resin LT-75 (20.0 g) with the hardener FM-260 (4.0 g) plus paraformaldehyde powder (2.0 g). The time period between addition of the PRF resin system and the gellation of the mixture was measured.

Sufficient amounts of material were formulated to make small-scale gluing tests. For Part I, each of the two extracts (14 g of A or B) was dissolved in water (20 g). Then, 1.2 g of a 50 percent sodium hydroxide solution was added to 15-g aliquots of these tannin solutions. For Part II, the modified commercial PRF adhesive described above for the gellation time studies was used. Eight g of the Part II resin was then combined with 8.0 g of the Part I tannin solution of the mixed system adhesive wood gluing tests. The remaining tannin extract solutions (containing sodium hydroxide) were evaluated in a "Honeymoon" system (8) by applying the Part I solutions to one face and an equal weight of the Part II PRF adhesive to the other face of the laminate.

The second adhesive batch was made in a larger quantity by combining the solid extract B (42 g) with water (60 g). A 50 percent sodium hydroxide solution (3.2 g) was added to this tannin solution to form one adhesive component. The second component, a PRF adhesive, was prepared by combining Borden's resin LT-75 (80 g), hardener FM-260 (16 g), and paraformaldehyde (8 g). These two components were combined in a series of blends ranging from PRF/extract B solution ratios of 50/50 down to 23/77 parts by weight.

Wood gluing

Gluing tests were made using selected and freshly planed Douglas-fir lumber 3/4 inch thick and 6 by 8 inches in gluing area. The wood had been conditioned at 65 percent relative humidity and 70°F for more than 6 months prior to use. Two laminates were bonded for each sample. The spread rate was not prescribed but was allowed to be self-adjusted by squeeze-out. The assemblies were closed and pressed immediately at 150 psi and 72°F overnight.

One such lay-up was made for each tannin-sulfonate/PRF combination. Each laminate was cut to yield six shear blocks of standard dimensions, 2 by 1-3/4 inches (1,2). In all cases, two blocks were sheared when dry (AITC T107), two blocks were sheared after water impregnation (AITC T110), and two blocks were sheared after boiling in water (no reference to an AITC Standard). Experience has shown that this combination of test procedures, followed by proper interpretation, gives valuable information for the development of wood adhesives.

TABLE 1. — *Bond quality of two laminates made with adhesives formulated by mixing sulfonated tannins with PRF resins at equal weights.*

Extract	A	B
Dry shear AITC-T107[a]		
Shear strength (psi)	1,773 1,697	1,323 1,640
Average[b]	1,735 (50)	1,480 (220)
Wood failure (%)	95 100	100 100
Average[b]	97 (4)	100 (0)
Vacuum-pressure soak AITC-T110[c]		
Shear strength (psi)	930 933	950 1,280
Average[b]		1,115 (230)
Wood failure (%)		100 100
Average[b]		100 (0)
2-hour boil[d]		
Shear strength (psi)	800 820	650 856
Average[b]	810 (15)	753 (145)
Wood failure (%)	90 85	95 90
Average[b]	88 (4)	92 (4)

[a]AITC T107 calls for dry shear strength and wood failure of 1,100 psi and 70 percent.
[b]Numerals in parentheses represent one standard deviation.
[c]Water impregnation according to AITC T110; blocks sheared wet but wood failure read after drying sheared specimens. Required minimum wood failure: 70 percent as per AITC 200-83 (p. 26) 5.2.4.2 and ANSI/AITC A190.1 (p. 9) 5.3.2; 80 percent as per ANSI/AITC A190.1 (p. 5) 4.5.2.1; 75 percent as per ASTM D-2559 (the equivalent ASTM test).
[d]Not a standard test.

Results and discussion

Extraction of whole southern pine bark with 4.0 percent sodium sulfite and 0.4 percent sodium carbonate (based on ovendry bark weight) at reflux for 2 hours gave total extract yields of 23.9 percent (20.2% of bark extract and 3.7% of inorganic chemical) as judged by measurement of the extract solids content and assuming that the bark suspension could be dewatered to 50 percent moisture content after extraction. The condensed tannin-sulfonate extracts were sufficiently soluble in water to permit solution concentrations of slightly over 40 percent solids without encountering excessively high viscosity. The viscosity of these solutions did not increase significantly when kept at ambient temperature over a period of 5 days. On addition of sodium hydroxide, the solution viscosity increased. An increase in viscosity would be expected because of loss of the sulfonate function and condensation of the quinone methide thus formed with the nucleophilic phloroglucinol rings of the tannins. Alkaline solutions of these extracts retained workable viscosities for up to 4 hours. If stored for longer periods of time, these solutions became firm gels or solidified.

When alkaline solutions of these extracts were combined with a PRF resin and additional paraformaldehyde, hard solids were obtained that showed little evidence of water solubility, judged by only slight coloration of water when the solids were soaked for several weeks. Gel times for these adhesives varied between 30 and 60 minutes at room temperature. Adhesives made with the extract A immediately formed lumps, and precipitates separated from the resin after several minutes of mixing. This adhesive was used for wood bonding even though some insoluble material was present. However, adhesives made from the roller-dried extract B remained smooth with good spreading properties over a period of about 15 minutes.

Use of either of these extracts to replace 50 percent of a PRF adhesive in laminating Douglas-fir lumber (by mixing the extracts with a modified PRF adhesive) resulted in gluebond quality exceeding minimum requirements of the AITC Standards for shear strength and wood failure after dry shear (ATIC-T107) (Table 1) (1,2). When these sulfonated tannins were used to replace the PRF adhesives in a two-component "Honeymoon" system, the bond quality was still good in both dry and wet shear and shear strengths were quite high (Table 2). Both shear strengths and wood failures decreased to below acceptable limits when these sulfonated tannins were used to replace PRF adhesives in amounts greater than 50 percent by weight (Table 3).

When considering the bond quality obtained with all 50 percent replacement resins together, one laminate had low shear strength and wood failure when tested after 2 hours of boiling. Even so, the average shear strengths when tested dry, after a vacuum-pressure water soak, and after 2 hours of boiling were 1,625, 1,021 and 762 psi respectively; all above AITC requirements. The average wood failures of 95, 93.5, and 81 percent after the above tests also were indicative of high quality bonds. When the shear strengths of the eight laminates in Tables 1 and 2 were pooled, the respective averages and standard deviations were 1,503 and 183 psi when tested dry, 872 and 227 psi when tested after vacuum-pressure soak, and 752 and 131 psi when tested after 2 hours of boiling. Corresponding averages and standard deviations for the wood failures were 98 and 2.4, 96 and 4.8, and 88.8 and 3.3 percent, respectively.

It must be emphasized that these results are from preliminary trials only and that even higher values with less variability or even higher dilution ratios may be possible by further refinement of the method of preparing extracts and/or the adhesive formulation. With the exception of one sample tested after 2 hours of boiling, the shear strengths of bonds made with the adhesives formulated with 50 percent condensed tannin

TABLE 2. — *Bond quality of laminates made using sulfonated tannins and PRF resins in "Honeymoon" systems.*[a]

Extract	A	B
Dry shear AITC-T107		
Shear strength (psi)	1,210 1,367	1,487 1,530
Average[b]	1,288 (110)	1,509 (30)
Wood failure (%)	95 100	100 95
Average[b]	97 (4)	97 (4)
Vacuum-pressure soak AITC-T110		
Shear strength (psi)	513 983	573 817
Average[b]		695 (170)
Wood failure (%)		95 85
Average[b]		90 (7)
2-hour boil		
Shear strength (psi)	683 960	750 503
Average[b]	822 (195)	626 (175)
Wood failure (%	90 85	90 85
Average[b]	88 (4)	88 (4)

[a]See Table 1 for required shear strength and wood failure.
[b]Numerals in parentheses represent one standard deviation.

TABLE 3. — *Effect of PRF to tannin ratio on gluebond quality of Douglas-fir laminates.*[a]

PRF/tannin ratio	AITC-T107	AITC-T110	2 hr. boil
	1,960 2,267	1,220 2,010	1,460 140
Average[b]	2,113 (240)	1,615 (560)	800
Wood failure (%)	85 80	85 80	82 18
Average[b]	82 (4)	82 (4)	50
40/60			
Shear strength (psi)	1,450 1,683	487 47	1,620 2,287
Average[b]		267	1,953 (470)
Wood failure (%)		62 18	100 100
Average[b]		40	100 (0)
Shear strength (psi)	2,080 1,750	200 Delam	760 130
Average[b]	1,915 (230)	100	445
Wood failure (%)	95 85	10 0	60 0
Average[b]	80 (7)	5	30
Shear strength (psi)	1,493 1,850	Delam Delam	650 90
Average[b]			370
Wood failure (%)			60 0
Average[b]			30

[a]See Table 1 for required shear strength and wood failure.
[b]Standard deviations (shown in parentheses) were not calculated where bond quality was far below requirements.

sulfonates and 50 percent PRF adhesives (Table 3) were extraordinarily high. The more drastic loss of bond quality shown in the modified AITC-110 as compared with the boiled samples suggests that adhesives made with high proportions of tannin sulfonates had not cured sufficiently prior to testing. It may be possible to increase the cure rate of these resins through adjustment of aldehyde content and resin pH and if so, it might be possible to replace even more of the synthetic PRF resin with extracts from southern pine bark.

Much work still needs to be done to identify the area of overall workable gluing compositions, taking into account bond strength, pot lives, spread levels, assembly times, range of gluing temperatures, and substrate moisture contents. Continuing research is certainly justified by the potential savings in resin costs that would result if 50 percent of a PRF resin could be replaced with a natural tannin readily available to the forest products industry.

Conclusions

Sulfite extracts of southern pine bark show great promise in their ability to replace about 50 percent of the PRF adhesive in cold-setting wood-laminating resins when applied either as mixed adhesives or in "Honeymoon" systems.

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